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Research Article

Investigating the Role and Scope of Catalysts in Inverse Vulcanization

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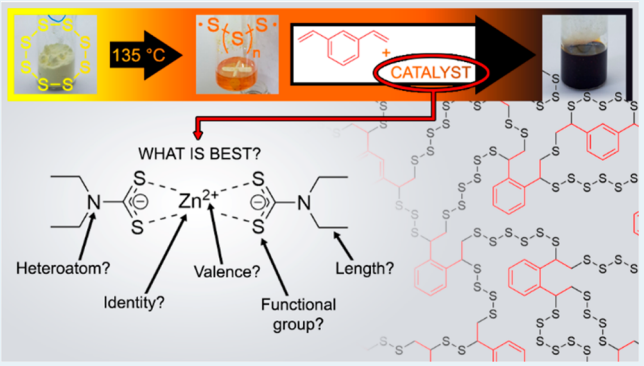
ABSTRACT: Inverse vulcanization is a potential route to the use of the large excesses of elemental sulfur, creating high-sulfur-content polymers with many potential applications. The addition of a metal diethyldithiocarbamate catalyst was previously found to bring several benefits to inverse vulcanization, making the process more attractive industrially. Herein is reported the establishment and exploration of a library of catalysts for inverse vulcanization. Three ranges of catalysts and up to 32 compounds and their combinations have been investigated. By trialing these alternative catalysts, several tentative deductions about the mechanism have been made. It has been found that stronger nucleophiles give a greater rate enhancement, but with the tradeoff that harder bases may promote hydrogen sulfide byproduct formation. Monomer binding by the cation may be a crucial mechanistic step, and it is possible that the catalysts act as phase transfer agents between the immiscible sulfur and organic phases. Additionally, the versatility of catalytic inverse vulcanization has been demonstrated with several different comonomer families.



KEYWORDS: *inverse vulcanization, catalytic, diethyldithiocarbamate, sulfur, mechanism, polymerization, cross-link*

INTRODUCTION

In order to mitigate acid rain, petrochemical feedstocks are purified of sulfurous compounds by means of hydrodesulfurization and the Claus process, yielding large quantities of elemental sulfur as a byproduct (more than 60 million tons per annum).[1−4] While a small portion of this sulfur is used to create fertilizers and sulfuric acid, among other applications, the supply of sulfur greatly outweighs the demand, leading to megaton quantities of sulfur being stored in open-air stockpiles with unexplored environmental consequences (Figure 1a).[4,5] These stockpiles of sulfur are expected to expand more rapidly in coming years, as the depletion of fossil fuels drives the use of previously avoided petrochemical resources that contain greater levels of sulfur contamination.

As such, elemental sulfur is a cheap, abundant, and underutilized resource, with wide availability for use in new applications.[4,5] In terms of materials chemistry, pure elemental sulfur can be self-polymerized, but the resulting homopolymer is unstable and depolymerizes back to the monomer, S_8 rings, upon cooling.[3] Inverse vulcanization allows the stabilization of sulfur chains to depolymerization, by the direct reaction of elemental sulfur with small-molecule organic polyenes.[6] To this end, inverse vulcanization is an avenue by which elemental sulfur may see appealing applications, on account of the properties of the product copolymers of this simple and facile polymerization of molten sulfur with divinyl comonomers (Figure 1b).[6] These inverse vulcanized polymers show promising applicability in the fields of electrochemistry, where they may act as cheap and effective cathode materials in lithium sulfur batteries; remediation of water, due to their ability to take up heavy metals such as mercury, and optics, where they may act as highly refractive and infrared-transparent components.[7,12−15]

There are many other fields were inverse vulcanized polymers may be applied; however, inverse vulcanization is not without its drawbacks.[16−19] Several potential comonomer molecules have been found to be unreactive in inverse vulcanization, with a significant example being the methacrylate-derived ethylene glycol dimethacrylate (EGDMA, Figure 1b), suggested to be a result of the electron-withdrawing conjugation of its double bonds to the neighboring carbonyl groups.[11] Furthermore, inverse vulcanization requires relatively high reaction temperatures, which has been shown to promote the formation of the toxic byproduct hydrogen sulfide, increase the risk of hazardous autoaccelerations (the Trommsdorff−

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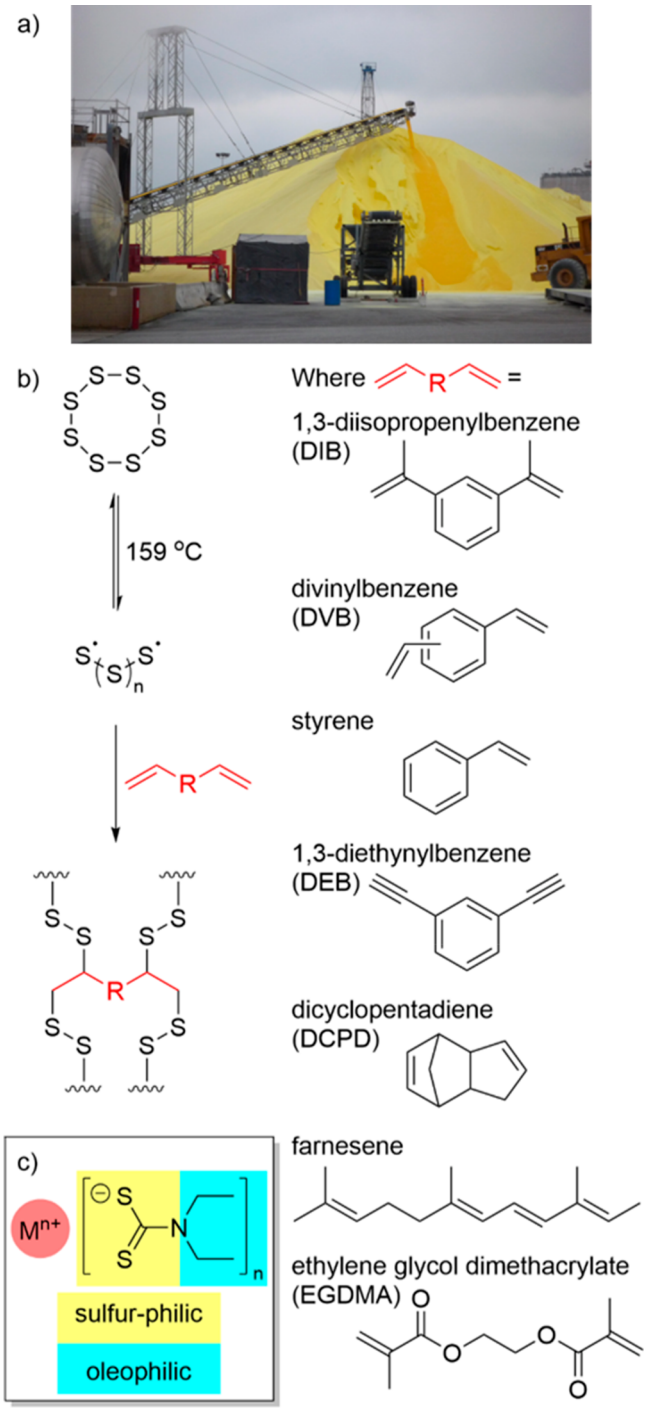


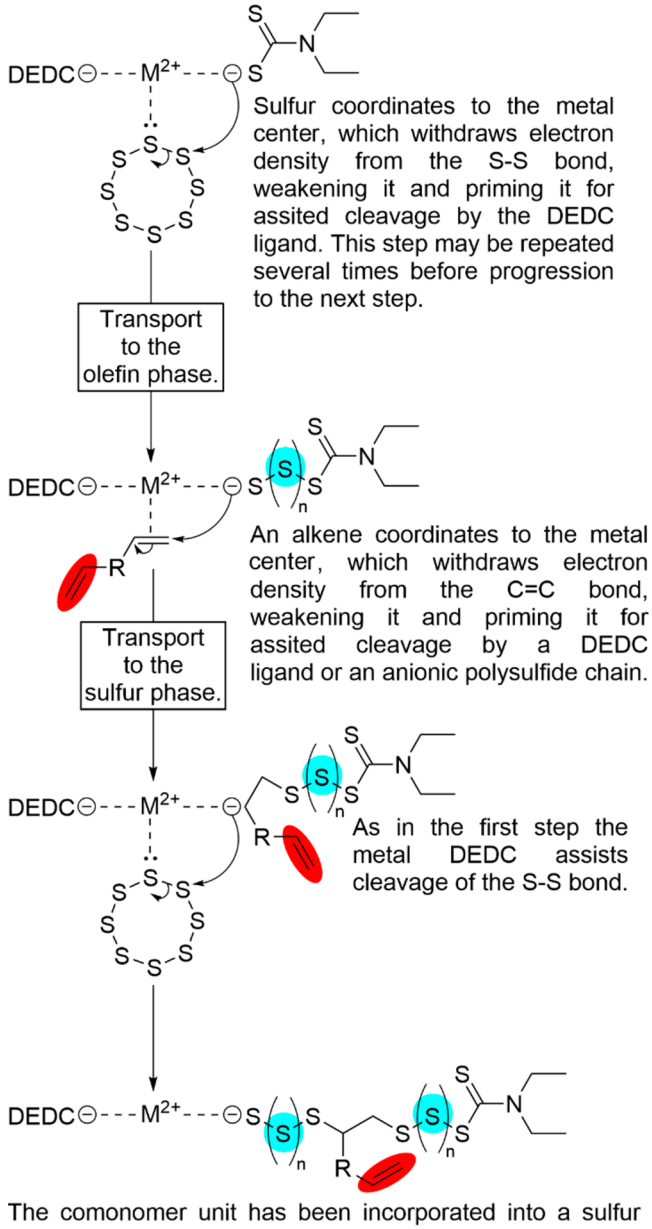
Figure 1. (a) A sulfur stockpile. (b) Generalized reaction scheme of inverse vulcanization and molecular structures of several example comonomers in inverse vulcanization. (c) Generalized molecular structure of a metal DEDC catalyst, with the proposed lyophilicities of its moieties.[7−11]

Norrish effect), and generally raise the cost of a reaction, as it requires more input thermal energy.[20] In addition to these drawbacks raising potential concerns for any prospective industrial level syntheses, the high temperatures also limit the variety of applicable organic comonomers to those that are largely involatile at the reaction temperatures.

Catalytic inverse vulcanization is a recent development which, by the inclusion of a metal diethyldithiocarbamate (DEDC) catalyst (Figure 1c), permits lower reaction temperatures, reducing the aforementioned drawbacks while providing new benefits, such as increased yields of reaction, a higher glass transition temperature (T_g) in the product polymers, and the polymerization of otherwise unreactive comonomers such as EGDMA.[11]

However, with catalytic inverse vulcanization's recent discovery, little is known about the mechanism. As discussed by Wu et al., it is still unclear as to whether metal DEDCs should be classed as true catalysts or as initiators or activators, because a pathway to their catalytic regeneration has not been identified. Nevertheless, Wu et al. proposed a mechanism for catalytic inverse vulcanization, consistent with their experimental observations (Scheme 1). First, it was found that

Scheme 1. Proposed Mechanism for Catalytic Inverse Vulcanization[11]



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metal-free molecules were poor catalysts, or noncatalytic, suggesting that a metal cation may be important for sulfur or comonomer binding. Second, catalytic inverse vulcanization permits lower reaction temperatures, which may be explained by the weakening of sulfur−sulfur bonds by coordination to the metal center, as the high temperatures of uncatalyzed inverse vulcanization are theorized to be necessary for homolytic sulfur−sulfur bond cleavage. Third, catalytic inverse vulcanization allows unreactive comonomers to be polymerized, which can be explained by coordination of the cation to the carbon−carbon double bonds of the comonomer, thereby providing a lower energy reaction pathway, though an alternative theory to direct binding of the monomers is a concerted mechanism. It was also proposed that the DEDC ligand may assist in the cleavage of sulfur−sulfur bonds and carbon−carbon double bonds by behaving as a nucleophile, further explaining why catalytic inverse vulcanization permits lower reaction temperatures. Finally, it was suggested that the metal DEDCs may act as phase transfer agents between the immiscible sulfur and organic phases, as the sulfur-containing dithiocarbamate group may have an affinity for the sulfur phase while the alkyl chains may have an affinity for the organic phase.[11]

Note that in Scheme 1 the alkene bonds highlighted in red are still reactive and that the sulfur chains highlighted in blue may still be prone to scission and further polymerization. The sulfur rings in this mechanism may be replaced with growing sulfur homopolymer chains or growing inverse vulcanized oligomers. The second DEDC ligand may also act as a nucleophile at any point in the mechanism. The mechanism has been portrayed here as anionic but could in fact be a radical mechanism or a mixture of both. Furthermore, the binding steps could occur instead as a concerted mechanism, which aligns better with the concept that coordination and activation of alkenes by first-row transition metals is uncommon, and evidence of this could not be found by NMR. Additionally for nonelectrophilic alkenes, which are not conjugated to an electron-withdrawing group, and so are not activated toward anions, a radical mechanism may be more probable.

Detailed here is the first study of the role that the metal DEDC catalyst plays in catalytic inverse vulcanization. Aspects of the catalyst's structure, with potential importance to different steps in the proposed mechanism, were varied in order to obtain alternative catalysts. For each alternative catalyst, predictions were made using Wu et al.'s proposed mechanism, as to whether the variation to the catalyst's structure would be beneficial or detrimental to the catalyst's activity. Whether these predictions were confirmed or disproved by the experimental results obtained from the catalytic trial provided evidence for or against each particular aspect of the mechanism. In doing so, a preliminary understanding of the mechanism of catalytic inverse vulcanization has been constructed, along with an initial understanding of what factors make a good catalyst. Herein, a library of catalysts has been compiled, which includes and compares various metal DEDC alternatives as well as a range of nonmetallic catalysts. Additionally, a brief study indicating the versatility of catalytic inverse vulcanization and its advantages has been completed.

RESULTS AND DISCUSSION

Standardized Method. As detailed in the Supporting Information, a rigorous method for the inverse vulcanization of sulfur and divinylbenzene (DVB) was developed to create consistent reaction conditions that would allow comparison of the results. Orme et al. also found that the reaction conditions were important with inverse vulcanization reactions involving DVB, further indicating that control over the reaction variables is crucial.[21] In short, this method was to add 5 g of DVB to 5 g of molten sulfur at 135 °C with 900 rpm stirring and then measure the time taken for the reaction solution to become too viscous to stir. After this the polymers were left on the hot plate at 135 °C overnight. DVB was selected to be the model organic comonomer because it is inexpensive, can undergo inverse vulcanization without a catalyst (useful for benchmarking), and may have negligible loss due to evaporation at the temperatures used. To quantify the volatility, neat DVB was heated without sulfur at 135 °C for 1 h (a typical vitrification time). The remaining mass of DVB was found to be 93.7 ± 0.3%, suggesting that a significant amount of DVB evaporates over the course of inverse vulcanization reactions and that the yield may be increased in reactions with shorter vitrification times due to the fact that there is less time for the DVB to evaporate before being incorporated into a polymer chain. The yield of uncatalyzed inverse vulcanization was found to be 91.7 ± 1.2%, lower than that of the DVB evaporation experiment, which suggests that there is some other loss to the yield. This loss cannot be due to the volatilization of sulfur because, after sulfur was heated for 1 h at 135 °C, the remaining mass was found to be 99.9 ± 0.0%, unsurprising given that the boiling point of sulfur is 445 °C.[22] See the Supporting Information for more details on the evaporation experiments.

The loss to the yield is instead attributed to hydrogen sulfide formation. Several reactions were repeated under gas capture conditions: the amount of hydrogen sulfide given off was quantified by bubbling the exhaust gases of the reactions through a solution of lead(II) acetate, which precipitates lead sulfide when it is exposed to hydrogen sulfide.[23] The precipitate was weighed to determine the amount of hydrogen sulfide given off by the selected reactions. For the uncatalyzed reaction, about 1.43 mmol of H_2S was found to be produced, equating to 48 mg or a 0.48% mass loss to the yield. This is not enough to account for the total loss in mass, as was the case for all gas capture reactions: none gave a H_2S quantity sufficiently large to account for the mass loss in the yield. However, it is strongly suspected that not all of the H_2S was captured (see the Supporting Information for details) and that the mass loss due to H_2S formation will be higher than what has been represented here.

Regardless, a qualitative comparison between the catalyzed and uncatalyzed gas capture reactions gave statistically significant results. It was found that a reaction catalyzed by $Zn(DEDC)_2$ gives off less hydrogen sulfide (0.93 mmol, 32 mg) in comparison to the equivalent uncatalyzed reaction, providing confidence that hydrogen sulfide formation is a loss to the yield and that catalysis minimizes this loss (Figure S12).

Once a robust method was established, the inverse vulcanization of DVB and sulfur was repeated numerous times with 0.28 mmol of various catalysts. A standard catalyst loading of 0.28 mmol was chosen, because it corresponds to a 1% weight loading (100 mg) of the previously most reported catalyst, $Zn(DEDC)_2$, in a 10 g scale reaction. The equivalent

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molar loading of all catalysts used corresponds to a molar ratio of approximately 137:70:1 in terms of DVB:S_8:catalyst.

For each reaction three main variables were used to judge the efficacy of a catalyst. The first of which was the vitrification time, defined as the time elapsed between the addition of the divinylbenzene (DVB) to the molten sulfur and the moment at which the reaction solution became too viscous for the stirrer to rotate. Video 1 in the Supporting Information shows a typical vitrification event and indicates how the triplicate reactions seize in rapid succession, giving rise to small standard deviations in the vitrification time data. A shorter vitrification time is indicative of a greater rate of reaction and a greater rate enhancement provided by the catalyst in question.

The second variable used to judge the efficacy of the catalysts was the yield of the reaction. Naturally, a higher yield is desirable, but this is even more so here, as an increased yield may mean fewer toxic hydrogen sulfide emissions. A higher yield may also be indicative of a facet of the mechanism, as it has been suggested that the formation of hydrogen sulfide is the result of hydrogen abstraction from the organic comonomer molecule; thus, a higher yield may indicate a catalyst that is more effective at suppressing hydrogen abstraction by providing a faster competing kinetic pathway for inverse vulcanization to occur by.[20]

The third variable by which the catalysts' efficacies were judged was the glass transition temperature (T_g) of the product polymers, obtained by differential scanning calorimetry (DSC). A more cross-linked polymer, with a more uniformly cross-linked structure, should have a higher T_g value. This is because the polymer structure increases in rigidity with increasing cross-linking, making it harder for the polymer chains to move over one another. Thus, more thermal energy is required to overcome this immobilization effect, giving a higher T_g value. Therefore, in this study, the T_g value is used as an indication of how cross-linked the polymer is and therefore how effective the catalyst is. A more effective catalyst may drive a reaction further toward completion and increase double-bond consumption, thereby increasing the cross-linking density and the T_g value. A more effective catalyst may also promote more uniform cross-linking if it acts as a phase transfer catalyst, as the reaction will no longer be constrained to only the phase boundaries, thus preventing microscopic regions of high cross-linking and regions of less cross-linking. Typical DSC thermograms of inverse vulcanized polymers that were synthesized in this work can be found in the Supporting Information. Note that none of the obtained DSC thermograms indicated the presence of unreacted sulfur when DVB was the organic comonomer, which would be evident from the melting transitions of crystalline S_8 regions at 95 and 115 °C.[22]

Additionally, the FTIR spectra of all polymers were recorded and compared to the FTIR spectrum of the neat organic comonomer used in their synthesis, usually DVB, to identify any characteristic peaks of unpolymerized vinyl bonds. Representative FTIR spectra can be found in the Supporting Information. Almost all polymer spectra contained extremely weak signals that could be ambiguously assigned to those of unpolymerized vinyl bonds, but due to the weak nature of these signals and the fact that all polymer spectra were nearly identical for a given organic comonomer, the FTIR analysis holds little diagnostic value in the judgment of each catalyst's efficacy. The insolubility of the produced polymers prohibited solution NMR.

Comparative Library of Tested Catalysts. Using the aforementioned method, numerous catalysts were trialled in inverse vulcanization. Table 1 compiles all the results of the catalytic trials into a library of tested catalysts, to allow easy comparison and selection of the catalysts by the community interested in applying inverse vulcanization. The results given here are presented as relative values for ease of comparison; absolute values are given in Table S6.

Table 1. Vitrification Times, Yields, and T_g Values of Catalytic Inverse Vulcanizations Relative to the Corresponding Uncatalyzed Inverse Vulcanization

reaction	relative vitrification time	relative yield	relative T_g
uncatalyzed	1.00	1.00	1.00
$Zn(DEDC)_2$	0.71	1.03	1.05
Na(DEDC)	0.42	1.04	1.07
Na(DEDC) + 15-crown-5	0.50	1.02	0.97
Ag(DEDC)	0.56	1.03	1.06
$Fe(DEDC)_3$	0.42	1.04	0.47
0.28 NH_4(DEDC)	0.87	1.02	1.04
0.56 NH_4(DEDC)	0.88	1.01	1.05
$Zn(DMDC)_2$	0.63	1.04	1.08
$Zn(DBDC)_2$	0.67	1.03	1.06
$Zn(DODC)_2$	0.63	1.01	0.90
$Mn(DEDC)_2$	0.41	1.01	1.04
$Fe(DEDC)_2$	0.66	1.04	1.04
$Co(DEDC)_2$	0.88	1.01	1.02
$Ni(DEDC)_2$	0.61	1.03	1.05
$Cu(DEDC)_2$	0.43	1.04	1.13
LiOH	0.92	0.94	1.01
NaOH	0.84	0.91	0.98
KOH	0.81	0.94	0.99
KEtX	0.77	1.02	1.03
KEtX + 18-crown-6	0.25	1.05	0.46
K^iPrX	0.79	0.97	0.97
K^iPrX + 18-crown-6	0.11	1.06	0.45
$PhSNH^tBu$	0.99	0.97	0.99
$HSC_{12}H_{25}$	0.89	0.95	0.95
$KSC_{12}H_{25}$	0.78	1.01	0.99
$KSC_{12}H_{25}$ + 18-crown-6	0.14	1.05	0.46
2-MBT	0.89	0.99	1.02
guanidine	0.91	0.96	1.00
thiourea	0.92	0.96	1.04
dodecylamine	0.80	0.98	1.05
dioctylamine	0.47	1.00	0.96
DABCO	0.62	1.01	0.91
18-crown-6	0.98	1.01	1.01

Benchmarks. The uncatalyzed inverse vulcanization of DVB was used as a control reaction, followed by catalytic inverse vulcanizations using $Zn(DEDC)_2$ and Na(DEDC) as benchmarks, since these are the two most detailed catalysts in Wu et al.'s previous work. Consistent with previous findings, both $Zn(DEDC)_2$ and Na(DEDC) decreased the vitrification time, improved the yield, and enhanced the T_g value of the product polymers (Figure 2). Further consistent with Wu et al.'s findings, Na(DEDC) was found to be the more effective catalyst, and this conclusion has been further reinforced in this work, as all the catalysts have been tested in equal molar quantities.[11] The finding that Na(DEDC) gives a greater rate enhancement than $Zn(DEDC)_2$, despite having one fewer

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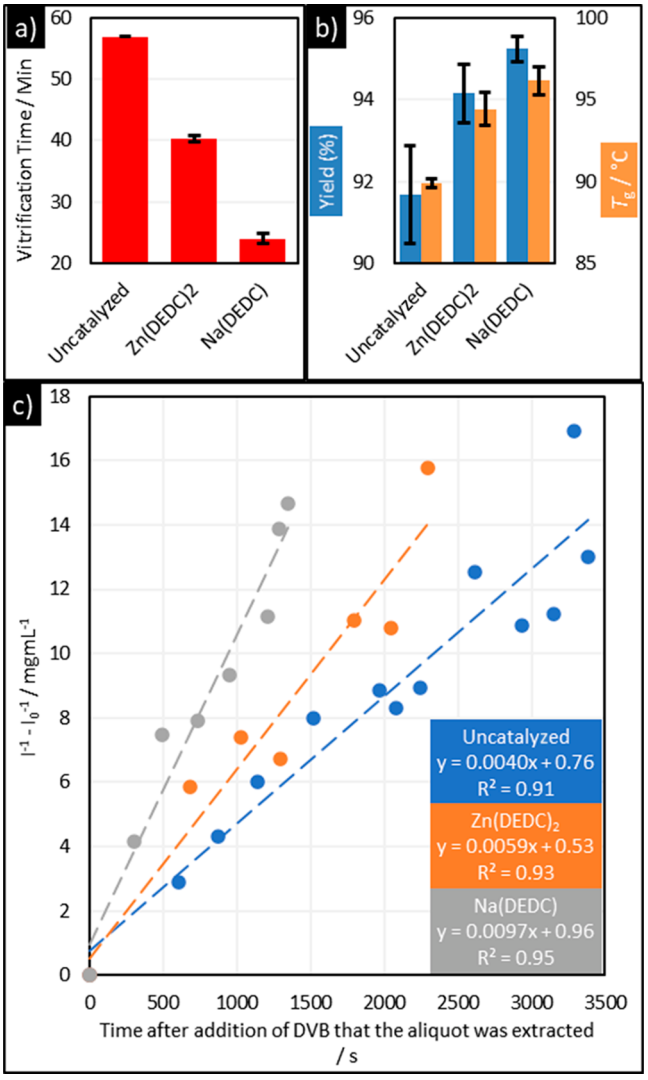

Figure 2. (a) Vitrification times, (b) yields and T_g values, and (c) NMR kinetics plots for an uncatalyzed inverse vulcanization and catalytic inverse vulcanizations using Zn(DEDC)$_2$ and Na(DEDC). See the Supporting Information for the meanings of I and I_0.

ligand, hints at the importance of the identity of the cation in the catalyst. There is, however, no certainty that these catalysts use the same mechanism, which may explain the significant difference in vitrification times between these two metal DEDCs.

To increase confidence that the vitrification time is a good measure of the rate of the reaction, an NMR kinetics experiment was performed upon the aforementioned inverse vulcanization experiments with no catalyst and Zn(DEDC)$_2$ and Na(DEDC) as catalysts. The results in Figure 2 and Table 2 show that the ratios of the second-order rate constants of loss of the alkene region peaks, corresponding to the reaction of DVB vinyl bonds, are comparable to the ratios of the inverse of vitrification times for the selected reactions. This suggests that the vitrification time is a good indicator of the rate of the reaction, which is simple and easy to measure. See the Supporting Information for details on the NMR kinetics experiment and the reasoning for why the ratios of the rate constants and the inverse of the vitrification times should be equal.

Cation Identity. Following on from the conclusion that the identity of the cation is of importance in the mechanism of catalytic inverse vulcanization, several catalysts were tested for their alternative cations: Ag(DEDC), a monovalent cation, Fe(DEDC)$_3$, a trivalent cation, and NH$_4$(DEDC), a non-metallic cation, the last of which was tested in both a 0.28 mmol loading and a 0.56 mmol loading (Figure 3).

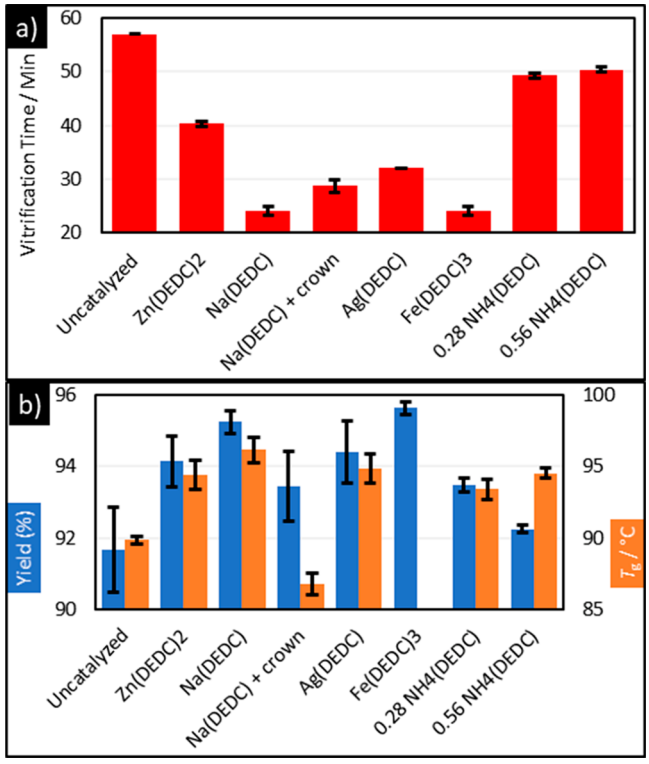

Figure 3. (a) Vitrification times and (b) yields and T_g values of inverse vulcanization and catalytic inverse vulcanizations using Zn(DEDC)$_2$, Na(DEDC), Na(DEDC) + 15-crown-5, Ag(DEDC), Fe(DEDC)$_3$, 0.28 mmol of NH$_4$(DEDC), and 0.56 mmol of NH$_4$(DEDC). The T_g value of Fe(DEDC)$_3$ is 41.8 ± 0.4 °C and is low due to the Trommsdorff−Norrish effect.

Table 2. Data from the NMR Kinetics Experiments

	reaction		
	uncatalyzed	Zn(DEDC)$_2$	Na(DEDC)
vitrification time^{-1}/min^{-1}	0.0175	0.0248	0.0417
ratio of vitrification time^{-1}	1	1.41	2.38
second-order rate constant from NMR kinetics ± standard error/ mg mL^{-1} s^{-1}	$3.96 \times 10^{-3} \pm 0.38 \times 10^{-3}$	$5.89 \times 10^{-3} \pm 0.74 \times 10^{-3}$	$9.65 \times 10^{-3} \pm 0.87 \times 10^{-4}$
ratio of the second-order rate constants	1	1.49	2.44

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NH_4(DEDC) was amenable to being tested in different mass loadings, as it was sufficiently poor as a catalyst that a higher loading did not induce the Trommsdorff−Norrish effect.

It is challenging to draw conclusions from the data regarding Ag(DEDC) and $Fe(DEDC)_3$, since it is impossible to vary the valence of the cation without changing the number of ligands. Nevertheless, the results of these tests further indicate that catalysts need not be limited to divalent cations, as both Ag(DEDC) and particularly $Fe(DEDC)_3$ surpassed $Zn(DEDC)_2$ in terms of their rate enhancements. It is worth noting that the case of $Fe(DEDC)_3$ highlights the fact that a catalyst which provides a greater rate enhancement is not necessarily the best choice from a practical perspective: after the stirrer stopped rotating, the $Fe(DEDC)_3$ reactions underwent the Trommsdorff−Norrish effect, which is known to cause rapid and inhomogeneous polymerizations that detrimentally affect the properties of the product polymers, explaining the poor T_g value (41.8 ± 0.4 °C) for this catalyst's product polymer. The vitrification time data for $Fe(DEDC)_3$ should still be valid and be unaffected by the Trommsdorff−Norrish effect, as the autoacceleration occurred after the stirrer had ceased to rotate. If a smaller loading of $Fe(DEDC)_3$ were to be used, then the Trommsdorff−Norrish effect could likely be avoided. Interestingly, as reported in the review by Fukuto et al., polysulfide anions, a potential reactive intermediate in catalytic inverse vulcanization, preferentially complexed to iron(III) over iron(II).[24] If polysulfide anions are present in catalytic inverse vulcanization, then this affinity for iron(III) may give some explanation as to why $Fe(DEDC)_3$ was such a powerful catalyst and why it was superior to $Fe(DEDC)_2$ in terms of vitrification time, the results for which will be discussed later on.

In contrast, NH_4(DEDC) gave relatively poor rate enhancements in both its 0.28 and 0.56 mmol loadings. This may be because NH_4(DEDC) has a nonmetallic cation which should lack the capability of monomer binding that metallic cations are capable of, suggesting that monomer complexation is an important part of the mechanism. An alternative explanation of NH_4(DEDC)'s poor rate enhancement, which also explains why the 0.56 mmol loading of NH_4(DEDC) gave a smaller rate enhancement than the 0.28 mmol loading, is that the ammonium cation acidifies the reaction, potentially deactivating any nucleophiles, such as polysulfide anions, that may be present in the reaction.[24,25] Though poor, NH_4(DEDC) still provided some rate enhancement, which suggests that, even if the cation is not capable of binding a monomer, the ligand will still have importance in the mechanism. This is also a reflection of the proposed mechanism that the ligand in the catalyst might aid the S_8-ring opening. As a final note on NH_4(DEDC), the yield data are complicated by the loss of ammonia from the catalyst during the reaction, and a further complication is that amines, including ammonia, can break sulfur−sulfur bonds and so may participate in the mechanism.[26,27]

To determine whether the sodium ion has importance in the mechanism of catalytic inverse vulcanization, 15-crown-5, which is a crown ether that is well-known to complex and capture the sodium ion, was used in an equimolar quantity with Na(DEDC). When a catalytic inverse vulcanization using Na(DEDC) was performed in the presence of an equimolar quantity of 15-crown-5, it was found that the vitrification time was longer than that when the 15-crown-5 was absent. This may be explained by the need for the sodium ion to be exposed to enable interaction with the monomers: when they are complexed to the sodium ions, 15-crown-5 ligands are likely to inhibit any interaction of the monomers. The reaction in the presence of 15-crown-5 was still significantly faster than that of the uncatalyzed inverse vulcanization of DVB, which suggests several possibilities: that there may still have been some free sodium ions, that interaction of the monomers to the sodium ions is not completely prohibited, or that the sodium ion is not essential in the mechanism but is assistive in achieving faster rates. How exactly the sodium ion interacts with the monomers and accelerates the reaction is unclear, since Lewis acidity in the sodium ion's behavior would be surprising, and this dissuades from the conclusion that the sodium ion is binding the monomers and may instead have an interaction that is not as yet identified. As such, Na(DEDC) may present some mechanistic differences from that proposed in Scheme 1. Further confidence in the importance of monomer binding as a mechanistic step can be found in the work presented by Draganjac et al., which details a variety of metal−ligand complexes that have polysulfide anions as ligands. Such complexes stabilize the formation of polysulfide anions while maintaining their reactivity.[25] These observations leave open the possibility of a concerted mechanism of the catalytic cycle in the presence of a metal cation—whereby the insertion of sulfur chain/fractions into the C−C covalent bond through the metal center and thereafter the dissociation of the newly formed C−S from the metal center occur simultaneously, requiring a low transitional energy for the transitional intermediates and furnishing a high reaction rate with low H_2S production.

Phase Transfer Agents. To further investigate the effect of the structure of the ligand upon the reaction, metal DEDCs with different alkyl chain lengths were trialed. Wu et al. theorized that the metal DEDC catalysts were behaving as phase transfer agents, using their dithiocarbamate moiety, which may interact favorably with the sulfur phase, to react with and bind sulfur. Then, via their oleophilic alkyl chains, the metal DEDC catalysts draw the bound sulfur into the organic phase, where it can react with cross-linker molecules more easily.[11] Krein et al. demonstrated the enhanced nucleophilicity of polysulfide anions with various α,β-unsaturated carbonyl compounds and showed that polysulfide anions were amenable to phase transfer catalysis.[28] Furthermore, the sulfur and organic phases of inverse vulcanizations normally show poor miscibility, and initially the reactions can be seen to be in two phases. The duration of this biphasic stage varied with comonomer identity, reaction temperature, and catalysis and lasted around 20 min for the benchmark reaction with no catalyst. When catalysis was present, the biphasic stage could be as short as 5 min. In higher temperature reactions, or reactions involving other cross-linkers, such as dicyclopentadiene, the biphasic stage was also drastically shortened.

Without a catalyst, it is likely that a reaction only occurs at the phase boundaries during the biphasic stage. As the reaction proceeds, organo-sulfur copolymer oligomers are formed, which increase the miscibility of the two phases until they become a single phase, which is observed in the later stages of the reaction. An amphiphilic catalyst may accelerate this process of enhancing phase miscibility. If this is indeed the case, then the length of the alkyl chains, and resultant oleophilicity of the catalyst, would be expected to influence the partitioning and therefore the reaction rate. To test this hypothesis, zinc dimethyldithiocarbamate ($Zn(DMDC)_2$, zinc diethyldithiocarbamate ($Zn(DEDC)_2$), zinc di-*n*-butyldithio-

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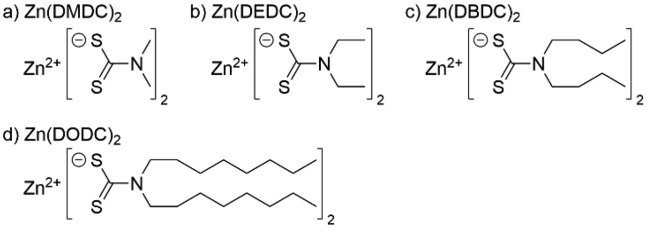
carbamate ($Zn(DBDC)_2$) and zinc di-*n*-octyldithiocarbamate ($Zn(DODC)_2$) were trialed in inverse vulcanization reactions (Chart 1).[29]

Chart 1. Molecular Structures of (a) Zinc Dimethyldithiocarbamate, (b) Zinc Diethyldithiocarbamate, (c) Zinc Di-*n*-butyldithiocarbamate, and (d) Zinc Di-*n*-octyldithiocarbamate



The results seen in Figure 4 show there is indeed a difference in vitrification time as a function of ligand alkyl

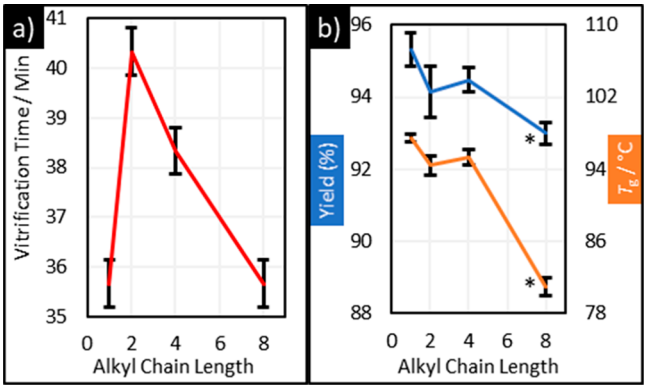


Figure 4. (a) Vitrification times and (b) yields and T_g values of inverse vulcanization and catalytic inverse vulcanizations using $Zn(DMDC)_2$, $Zn(DEDC)_2$, $Zn(DBDC)_2$, and $Zn(DODC)_2$. Data points marked with an asterisk have been detrimentally affected by the Trommsdorff–Norrish effect.

chain length, though it is not straightforward. For a chain length of two, four, or eight carbon atoms, the vitrification time decreases with increasing alkyl chain length. This increase in rate would be consistent with an increase in oleophilicity leading to improved phase transfer or compatibilization. The rapid inverse vulcanization in the presence of $Zn(DMDC)_2$ does not follow this trend but could potentially be related to its short alkyl chains allowing more rapid diffusion. It is unknown why $Zn(DODC)_2$ induced the Trommsdorff–Norrish effect during the curing step, rendering its yield and T_g data invalid, as several other catalysts had significantly shorter vitrification times and showed no evidence of the Trommsdorff–Norrish effect. As a final note, the effect of changing the alkyl chain length is relatively small in comparison to the effect of some of the other aspects of the catalyst that have been varied. This may be because the alkyl chain length is only important in the initial biphasic stage of the reaction.

First-Row Transition-Metal DEDC Catalysts. The aforementioned results strongly suggest that the identity of the metal cation is of importance in the mechanism of catalytic inverse vulcanization. Therefore, a series of period 4 d-block cation based catalysts, $Mn(DEDC)_2$, $Fe(DEDC)_2$, $Co(DEDC)_2$, $Ni(DEDC)_2$, $Cu(DEDC)_2$, and $Zn(DEDC)_2$, were tested in inverse vulcanization reactions to investigate the effect of changing the metal ion itself while keeping the ligands and the conditions constant. It was expected that the softness of the metal cation would affect the strength of coordination of the monomers, although several other factors, such as orbital vacancies and complex geometry, may also influence the results. Unfortunately, the syntheses of $Mg(DEDC)_2$ and $Ca(DEDC)_2$, two catalysts that would provide a more straightforward probe of the softness, were failures.[30,31]

On observation of Figure 5a, the vitrification time rises and then falls from left to right across the periodic table, finally

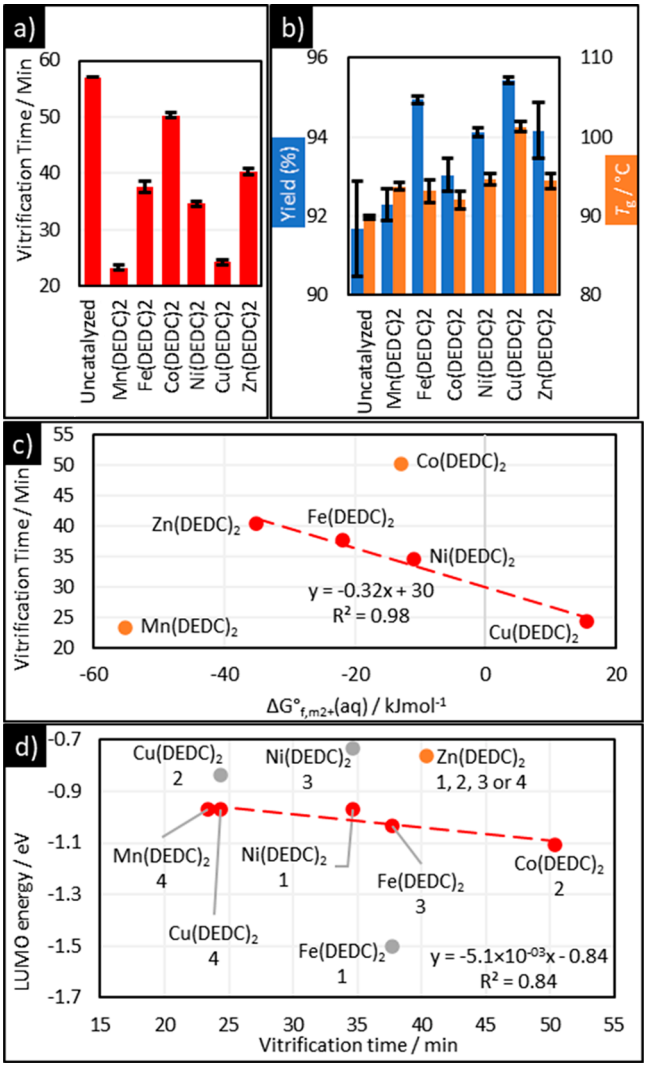


Figure 5. (a) Vitrification times and (b) yields and T_g values of inverse vulcanization and catalytic inverse vulcanizations using $Mn(DEDC)_2$, $Fe(DEDC)_2$, $Co(DEDC)_2$, $Ni(DEDC)_2$, $Cu(DEDC)_2$, and $Zn(DEDC)_2$. (c) Vitrification times against the $\Delta G^\circ_{f,m2+}(aq)$ values for the d-block metal cation DEDCs.[32] (d) Vitrification times against the calculated LUMO energy for the d-block metal cation DEDCs, with the multiplicities specified. Note that for $Zn(DEDC)_2$ the HOMO and LUMO energies were the same for each multiplicity.

increasing again upon reaching zinc, which could be a result of zinc(II) having a complete d subshell. When the vitrification time is plotted against the $\Delta G^\circ_{f,m2+}(aq)$ value, which may be used as a natural index of the softness of the cation, that is a more positive value indicates a softer cation, a tentative trend

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emerges.[32] Figure 5c indicates that, to some extent, a softer cation gives a faster vitrification time, with manganese(II) and cobalt(II) being outliers to this trend. One potential reason for $Mn(DEDC)_2$'s deviation from the trend may be due to decomposition of the catalyst during the reaction, as it was found that, when $Mn(DEDC)_2$ was heated to 100 °C for 1 h, it had decomposed from a burgundy powder to a brown sludge, which had an IR spectrum significantly different from that of $Mn(DEDC)_2$ (Figure S7). Additionally it was found that $Mn(DEDC)_2$ decomposed from a burgundy powder to a pale brown powder over the course of months under ambient conditions.

The other first-row transition-metal catalysts, including $Fe(DEDC)_3$, did not thermally decompose. No explanation as to why $Co(DEDC)_2$ deviates from the trend can be given at this time. It is possible that $Mn(DEDC)_2$ and $Co(DEDC)_2$ use alternative mechanisms in comparison to the other metal centers, but no evidence or explanation for this can be found. Regardless, given that two of the six reactions' vitrification times must be ignored to acquire this trend, it cannot be stated with any confidence that the vitrification time is linked to the cation softness, and it may be that the trend in Figure 5c is a coincidence. However, it can be noted that copper(II) diethyldithiocarbamate gave the best performance of all of the tested catalysts, if equal weighting is given to the three factors of rate, yield, and T_g. This could well be related to copper being the softest of the cations tested, giving rise to preferential interactions with sulfur.

Since no definite trend could be established with confidence regarding the cation softness, other potential trending factors were investigated that were not linked to the cation softness. The efficacies of the catalysts above may depend on their orbital energies, such as the HOMO energy, LUMO energy, or HOMO−LUMO gap, and it was hoped that these factors would give a clearer trend with the vitrification times. Attempts to determine the HOMO and LUMO energies experimentally by means of cyclic voltammetry gave no clear trend with the vitrification time. The detailed electrochemistry data is reported in the Supporting Information. Instead, the HOMO and LUMO energies were calculated using density functional theory, the details of which can be found in the Supporting Information. As shown in Figure 5d, a plausible trend was found between the vitrification time and the LUMO energy, if the value for $Zn(DEDC)_2$ was ignored. $Zn(DEDC)_2$ may deviate from this trend on account of its complete d subshell, and so its LUMO will not be a d orbital, providing a valid reason for it not to adhere to the trend. This suggests that the LUMO energy influences the vitrification time of the metal d-block catalysts. However, this trend is not without its theoretical weaknesses. Several of the metal DEDCs converged to unexpected geometries, namely square planar, which cannot be explained. Furthermore, several multiplicities gave computational results for the HOMO and LUMO energies; which multiplicity the complexes adopt in reality is difficult to determine. Other factors affecting the efficacy of the catalyst could include the metal−sulfur binding energy, which may influence the association and dissociation energies.

It should be noted that evidence of organic comonomer binding by several different catalysts could not be detected by NMR for various catalyst to comonomer molarity ratios, aligning with the conclusion that first-row transition metals do not usually coordinate alkenes and that the mechanism in Scheme 1 may adhere to a concerted pathway. Computational calculations provided further evidence that the metal centers do not bind the organic comonomer via the carbon−carbon double bond π orbital. $Zn(DEDC)_2$ and $Cu(DEDC)_2$, the latter being the most powerful of the metal DEDC catalysts, were modeled with DVB coordinated to the metal center through the π orbital of a nonaromatic carbon−carbon double bond. These calculations converged to structures where DVB was totally dissociated from the metal center, even when the starting structure had the DVB molecule explicitly bound as a ligand. The computational chemistry data revealed that there was no energy minimum at all where DVB was coordinated to the metal complex. This suggests that the metal center does not bind the organic comonomer through the reactive carbon−carbon double bond and that the mechanism of catalytic inverse vulcanization does not include such a binding as a step.

Hydropolysulfides and Polysulfide Anions. In addition to the metal DEDCs themselves and their identities, there are several other potential aspects to the mechanism of catalytic inverse vulcanization. One such aspect may be hydropolysulfides, polysulfide anions, and their related metal polysulfide complexes. Hydropolysulfides and their deprotonation products are reactive species which could be intermediates in catalytic inverse vulcanization. The IUPAC gold book defines a hydropolysulfide as "compounds having the structures RS_2H, $RS_3H\cdots RS_nH$, in which S_n is a chain of sulfur atoms, and R is hydrocarbyl".[33] Thus a polysulfide anion is any such deprotonation product of a hydropolysulfide. The literature precedent on hydropolysulfides is limited and finely dispersed, as they have received no dedicated research efforts because they are difficult to store.[24] One review by Fukuto et al. reports that hydropolysulfides are most easily generated from deprotonated hydrogen sulfide (HS^-) or thiolates, both of which exist in appreciable quantities in solution due to their pK_a values of 6.8 and 8−9, respectively.[24] These deprotonated species attack on other sulfur-containing species, like RSSR, to extend their chain length. In terms of catalytic inverse vulcanization, a metal DEDC could assist in the production of precursors to hydropolysulfides or even replace the precursors entirely and directly generate the hydropolysulfides themselves by attacking on sulfur. The review by Fukuto et al. goes on to describe that hydropolysulfides are more acidic than their single-sulfur counterparts and readily form polysulfide anions.[24] These polysulfide anions have enhanced nucleophilicity in comparison to their analogous thiolates, which would give them enhanced reactivity as intermediates in catalytic inverse vulcanization. Furthermore, these polysulfide anions are better one-electron donors in comparison to their single-sulfur analogues and so would be better able to promote a radical mechanism as well as an anionic mechanism, in line with the theory proposed by Lian et al. that conventional vulcanization may have both anionic and radical pathways.[34] Additionally, polysulfide anions are good ligands to a wide range of metal centers.[24,25] The review by Fukuto et al. showed evidence that polysulfide anions preferentially complexed to iron(III) over iron(II), which may explain the superior rate enhancement provided by $Fe(DEDC)_3$ over $Fe(DEDC)_2$. Another review by Draganjac et al. details a wide range of metal polysulfide complexes, almost all of which had enhanced stability in comparison to the free polysulfide anion but still maintained their reactivity, suggesting that they would be accessible and reactive intermediates in catalytic inverse vulcanization.[25] Krein et al. demonstrated the nucleophilic behavior of polysulfide anions by showing their reactions with

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various α,β-unsaturated carbonyl compounds that, in some cases, generated polymers as products.[28] Interestingly Krein et al. showed that polysulfide anions were amenable to phase transfer catalysis, which may provide confidence in the phase transfer action of metal DEDCs in catalytic inverse vulcanization.[28] More recently, Shin et al. demonstrated that polysulfide anions could easily be generated by the reaction of sulfur and Na_2S and that the aqueous polysulfide anions were reactive toward a divinyl compound, divinyl sulfone.[35] Though divinyl sulfone is a vinylic compound, the intensely electron withdrawing sulfone group activates the carbon−carbon bonds to nucleophilic attack in a conjugate addition manner. Therefore, drawing comparisons between this and the classic vinyl compounds of inverse vulcanization, which are typically nonelectrophilic, may not be appropriate.[35] Several literature sources detail methods for the synthesis of metal polysulfide complexes, many of which require only elemental sulfur and a metal complex to be mixed together, sometimes even at room temperature.[36−41] McDonald et al. used molybdenum complexes with dithiocarbamate ligands, the same ligands as the metal DEDCs, to synthesize molybdenum polysulfide complexes, using only elemental sulfur in refluxing acetone.[41] This provides confidence that metal polysulfide complexes may form from the metal DEDC catalysts under inverse vulcanization conditions, giving a plausible route to the generation of reactive polysulfide anions in catalytic inverse vulcanization, which would benefit from the aforementioned enhanced stability and maintained reactivity. Finally, Jung et al. found direct evidence that metal DEDCs can coordinate nucleophiles such as amines, which suggests that the theory of polysulfide anion complexation to a metal center could indeed stretch to metal DEDCs.[30] Metal DEDC catalysts may therefore form metal polysulfide complexes under inverse vulcanization conditions, and these complexes may be reactive intermediates in the catalytic pathway.

Proving the formation of such metal polysulfide complexes under inverse vulcanization conditions is challenging. Nevertheless, sulfur was reacted with a series of metal DEDCs, under inverse vulcanization conditions, and the products were characterized by PXRD. Although some experimental observations suggested the formation of metal polysulfide complexes, and new diffraction peaks not found in the starting materials were found in some cases, the results were not conclusive and metal polysulfides as intermediates in catalytic inverse vulcanization is an area that should receive further scrutiny by future research (see Figures S21−S27 in the Supporting Information for details and diffraction patterns).

To provide some confidence that polysulfide anions could attack the organic comonomers of inverse vulcanization, computational chemistry was employed. The nucleophilic attack of S_4^{2-} on two organic comonomers was modeled. The first was methyl methacrylate, a simplified and therefore less computationally demanding version of EGDMA. EGDMA was of interest here because its double bond is in conjugation to an electron-withdrawing ester group and so should be primed to accept nucleophilic attack in a conjugate addition manner. The second organic comonomer of choice was DVB, because it is electron-rich and therefore may be less prone to acting as an electrophile. Additionally, nucleophilic attack on DVB would yield a carbanion. Carbanions are typically high-energy species that are not stable, even though the negative charge could delocalize into the aromatic ring in the case of DVB. This argument can be offset by the fact that this species is a catalytic intermediate and needs to have a somewhat high energy, otherwise it would be unreactive and poorly active in a catalytic pathway.

The computational experiments detailed in the Supporting Information yielded total electronic energies for the attack of S_4^{2-} on methyl methacrylate and separately DVB. These total electronic energies do not take into account several thermodynamic factors such as entropic contributions but may be able to give some qualitative indication of the activation energies for nucleophilic attack. Nevertheless, these calculations gave electronic activation energies of 8.4 kcal mol^{-1} for methyl methacrylate and 1.5 kcal mol^{-1} for DVB, with transition state geometries that were confirmed by result of a negative frequency (imaginary mode) associated with the motion of bond-forming (see the Supporting Information for reaction coordinates). These values are comparatively small for activation energy values, which further reinforces the need to evaluate them qualitatively. The result of these calculations suggest that, when it is modeled under a vacuum, S_4^{2-} should readily bind to EGDMA and DVB, when the electronic energies are considered. DVB has the lower electronic activation energy, suggesting it would bind most readily, which is a surprising result that could stem from resonance stabilization of the negative charge. Further optimizations, such as the inclusion of solvent molecules in the calculations, would likely achieve more reliable values for the true activation energies but would require intensive computational work.

Inorganic Catalysts. As mentioned above, Shin et al. found that Na_2S could react with sulfur to produce polysulfide anions that are then capable of polymerizing with alkenes.[35] Thus, Na_2S was trialed here as a comparison to the metal DEDC catalysts. It is worth noting that, since the structure of Na_2S is significantly different from those of the metal DEDC catalysts, they likely function according to different mechanisms. Na_2S, by comparison to metal DEDC catalysts, was found to be quite a poor catalyst in inverse vulcanization, providing a vitrification time of 49.3 ± 0.3 min, only a few minutes shorter than that for the uncatalyzed inverse vulcanization of DVB, and a yield and T_g value of 92.8 ± 0.4% and 91.9 ± 0.1 °C, respectively, marginally higher than those for the uncatalyzed reaction.

Three more inorganic species, LiOH, NaOH, and KOH, were tested to allow an assessment of the effects of basicity.[42] Figure 6a shows that with decreasing pK_b comes a greater rate enhancement, suggesting that stronger bases can accelerate the inverse vulcanization process more, possibly by the formation of polysulfide anions.[24,25] This finding is consistent with the conclusion that NH_4(DEDC) was acidifying the reaction when it was present in greater quantities, thus slowing the reaction. Where LiOH, NaOH, and KOH were used as catalysts, the yield of the reaction in all cases was found to be lower than the yield of uncatalyzed inverse vulcanization. This may be explained by these reactions generating more H_2S gas in comparison to the uncatalyzed inverse vulcanization reaction. Evidence of this was found when the KOH reaction was repeated under gas capture conditions and was found to produce more hydrogen sulfide in comparison to the uncatalyzed inverse vulcanization of DVB, 1.55 mmol vs 1.44 mmol of H_2S (Figure S12).

Dithiocarbamate Alternatives. Potassium ethyl xanthogenate (KEtX) and potassium isopropyl xanthogenate (K^iPrX) have structural similarities to the dithiocarbamates (Scheme 2). KEtX can be used as an alternative to Na(DEDC)

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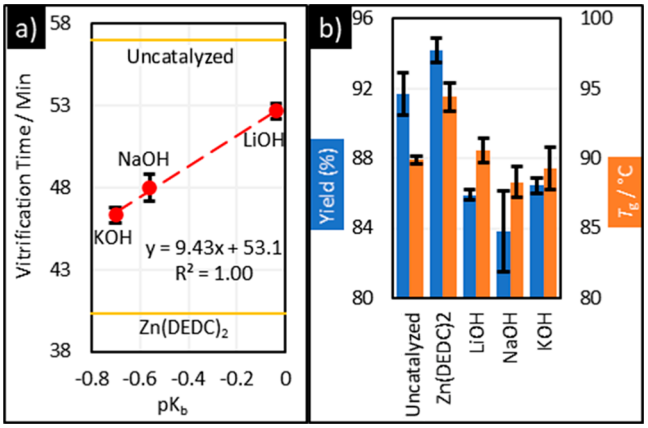


Figure 6. (a) pK_b vs vitrification time for three alkali-metal hydroxides and (b) the yield and T_g values of product polymers of inverse vulcanization and catalytic inverse vulcanizations using $Zn(DEDC)_2$, Na(DEDC), LiOH, NaOH, and KOH.[42]

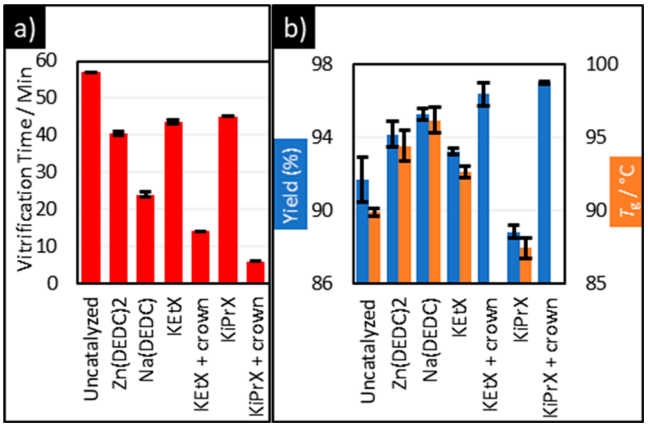
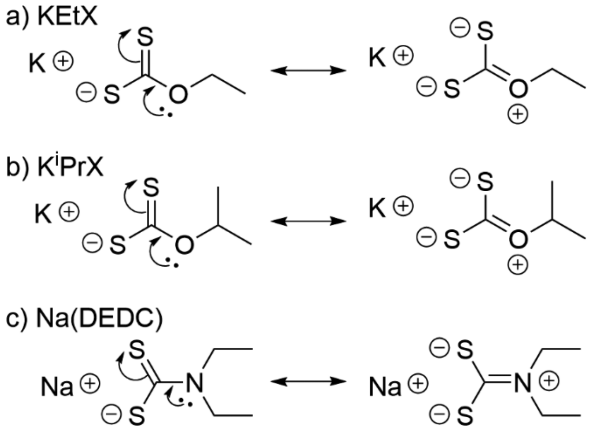


Figure 7. (a) Vitrification times and (b) yields and T_g values of inverse vulcanization and catalytic inverse vulcanizations using $Zn(DEDC)_2$, Na(DEDC), KEtX, KEtX in the presence of an equimolar quantity of 18-crown-6, K^{i}PrX, and K^{i}PrX in the presence of an equimolar quantity of 18-crown-6. The T_g values for KEtX in the presence of an equimolar quantity of 18-crown-6 and K^{i}PrX in the presence of an equimolar quantity of 18-crown-6 are 41.7 ± 1.9 and 40.9 ± 2.6 °C, respectively, and are low due to the Trommsdorff–Norrish effect.

Scheme 2. Molecular Structures and Alternative Resonance forms of (a) Potassium Ethyl Xanthogenate, (b) Potassium Isopropyl Xanthogenate, and (c) Na(DEDC)



to generate carbamoyl radicals.[43] Figure 7a shows that both KEtX and K^{i}PrX provided nominal rate enhancements in comparison with $Zn(DEDC)_2$ but were significantly slower than Na(DEDC). Although a comparison is complicated by the difference in cations between Na(DEDC) and the two xanthogenates, the lower rate enhancement provided by the xanthogenates may be attributed to the fact that they each possess one fewer alkyl chain than Na(DEDC), hampering their ability to act as phase transfer agents. An alternative explanation may relate to the electron-donating power of oxygen and nitrogen. Since nitrogen is widely considered to be more effective in donating its lone pair in comparison to oxygen, the dithiocarbamate nitrogen may donate more electron density to the sulfur atoms than the corresponding oxygen of a xanthogenate (see Scheme 2). The slightly longer vitrification time of K^{i}PrX in comparison to KEtX could be attributed to the bulkier isopropyl group causing slightly more steric hindrance, though this conclusion is made cautiously, considering how close the vitrification times are, despite being statistically significant. Interestingly, when KEtX and K^{i}PrX were used as catalysts in the presence of an equimolar quantity of 18-crown-6 (which gave a negligible rate enhancement when it was used as a catalyst alone), their vitrification times were drastically shortened, to the point where the Trommsdorff–Norrish effect occurred, suggesting that complexation of the potassium ion by the crown ether activates the xanthogenate. This result is in stark contrast to the result obtained when Na(DEDC) was reacted in the presence of 15-crown-5, which hindered the reaction. This suggests that the dithiocarbamates and the xanthogenates operate by different mechanisms, indicating that the identity of the nonsulfur heteroatom is more important than anticipated. The work performed by Jung et al. may give some explanation for this, as their work suggests several mechanistic pathways where the dithiocarbamate carbon is directly attacked and is involved in molecular transformations.[30] Since the nonsulfur heteroatom of the dithiocarbamates and the xanthates is bonded to this carbon, it would be expected to influence its behavior. The work by Jung et al. also indicates that steric hindrance plays a significant role in the attack upon this center, providing some backing to the theory that increased steric hindrance about K^{i}PrX is responsible for its slightly slower rate.[30]

Metal-Free Catalysts. Encouraged by the catalytically active organic species in the reaction, including DXDC (X = M, E, B, O), EtX, iPrX, and hydropolysulfides, a series of organo-catalysts were examined for activity in the inverse vulcanization reaction. Metal-free catalysts for inverse vulcanization would be beneficial because they avoid metal contamination of the product polymers, which may raise concerns about toxicity. Additionally, they may offer cost savings and pose fewer issues with renewability, as there are concerns that supplies of some metals may be depleted. Thus, the metal-free catalysts shown in Chart 2 were trialed in inverse vulcanization reactions, the results of which can be seen in Figure 8. Many of these catalysts were ineffective in decreasing the vitrification time. Of note, *N-tert*-butylbenzene sulfenamide (PhSNH^{t}Bu), a radical initiator, provided essentially no rate enhancement at all, resulting from its boiling point of 60 °C.

Dodecanethiol has a solubilizing alkyl chain and contains sulfur, even though its functional group is different from that of a dithiocarbamate. Thiols are widely regarded as good

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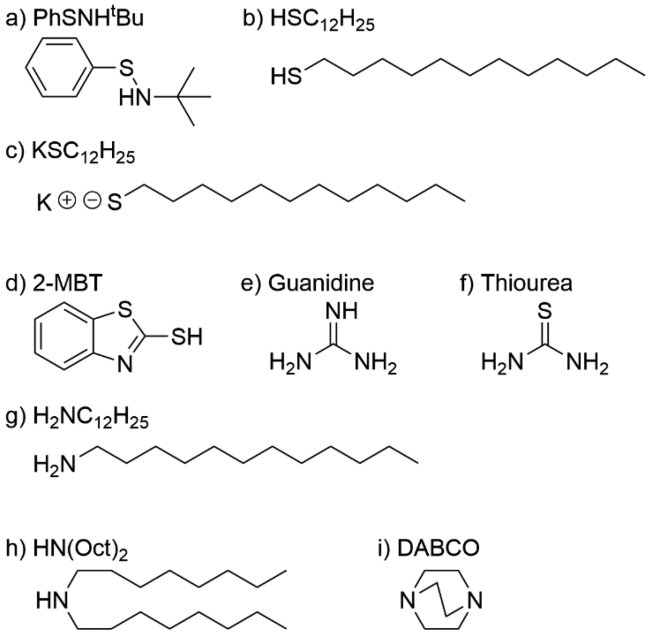
Chart 2. Molecular Structures of (a) *N-tert*-Butylbenzene Sulfenamide, (b) Dodecanethiol, (c) Potassium Dodecanethiolate, (d) 2-Mercaptobenzothiazole, (e) Guanidine, (f) Thiourea, (g) Dodecylamine, (h) Dioctylamine, and (i) 1,4-Diazabicyclo[2.2.2]octane



nucleophiles that can be further enhanced in nucleophilicity by deprotonation to the thiolate form. However, dodecanethiol was found to be quite a poor catalyst, as it provided a small but significant rate enhancement, perhaps through phase compatibilization alone. Potassium dodecanethiolate was found to be a significantly better catalyst in comparison to dodecanethiol, which may be a result of the enhanced nucleophilicity of the sulfur atom in its anionic state. Potassium dodecanethiolate, however, is not a metal free catalyst and it is unproven if the potassium cation that accompanies the thiolate has a coordinating effect as is suspected for the other metal dithiocarbamates. Nevertheless, it seems that, where a sulfur atom is the nucleophilic center of the catalyst, an anion seems to be superior to a neutral sulfur. This conclusion is supported by the relatively poor catalytic activity of 2-mercaptobenzothiazole (2-MBT), which was tested because its functional group resembles a dithiocarbamate but lacks a metallic cation. An additional reason that may explain 2-MBT's poor catalytic activity is its lack of an anionic charge, rendering it a weaker nucleophile. Such a conclusion is supported by the faster rate of reaction in the case of potassium dodecanethiolate over dodecanethiol. Interestingly, dodecanethiol gave a polymer with a poor yield and low T_g value in comparison to the uncatalyzed reaction, despite the rate enhancement, and potassium dodecanethiolate provided a polymer with high T_g and good yield. This may suggest that an anionic mechanistic pathway is what suppresses hydrogen sulfide evolution and provides polymers with high T_g values, consistent with the theory proposed by Lian et al. that conventional vulcanization proceeds by a radical and an anionic pathway that run simultaneously.[34] The yield and T_g provided by 2-MBT, which was nonionic, were not statistically significant from those of the uncatalyzed inverse vulcanization of DVB. When potassium dodecanethiolate thiolate was used as a catalyst in the presence of an equimolar quantity of 18-crown-6, the reaction was

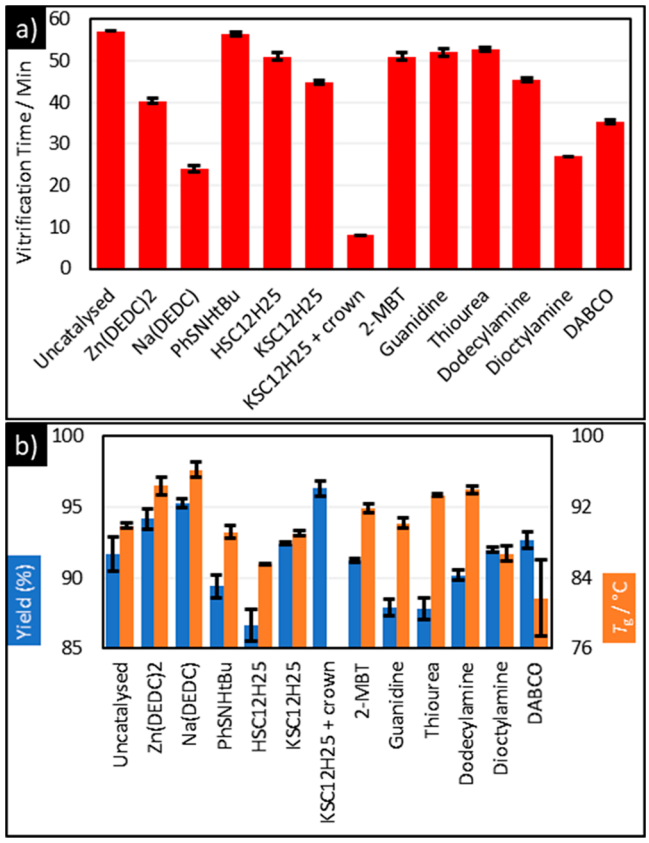


Figure 8. (a) Vitrification times and (b) yields and T_g values s of inverse vulcanization and catalytic inverse vulcanizations using Zn(DEDC)$_2$, Na(DEDC), PhSNH^{t}Bu, dodecanethiol, potassium dodecanethiolate, and potassium dodecane thiolate in the presence of an equimolar quantity of 18-crown-6, 2-MBT, guanidine, thiourea, dodecylamine, dioctylamine, and DABCO. The T_g value for potassium dodecane thiolate in the presence of an equimolar quantity of 18-crown-6 is 41.1 ± 1.6 °C and is low due to the Trommsdorff–Norrish effect.

accelerated to the point of the Trommsdorff–Norrish effect, similarly to those reactions of KEtX and K^{i}PrX in the presence of 18-crown-6. Here this can be simply explained as the crown ether enhancing the nucleophilicity of the thiolate by complexing the potassium counterion.

Guanidine and thiourea lack alkyl chains entirely but still consist of a central carbon atom singly bonded to two heteroatoms and double-bonded to one heteroatom, analogous to the dithiocarbamate group. Both gave rate enhancements, attributed to some nucleophilic behavior, but the rate enhancements were statistically insignificant from one another, indicating that the presence of a single nonionic sulfur atom did not have a significant effect upon the rate enhancement of the catalyst. Interestingly, Jung et al. reported that thioureas can be thermal decomposition products of metal DEDCs.[30] Because of the poor rate enhancement provided by thiourea itself and the superior rate enhancements provided by all metal DEDCs, it seems unlikely that a decomposition to thioureas is an important pathway in enhancing the rate of inverse vulcanization. It should be noted that the guanidine was used as a hydrochloride salt, and this work has already highlighted that acidification of the reaction may deactivate catalysis. The poor activity of these two catalysts is attributed to their lack of anionic moieties and their lack of solubilizing

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Table 3. Vitrification Times, Yields and T_g Values of Inverse Vulcanizations and Catalytic Inverse Vulcanizations with Different Catalysts, Feed Ratios, Alternative Cross-Linkers and Varied Temperatures[a]

cross-linker	sulfur:cross-linker mass ratio	temp of reaction and curing stage/°C	catalyst (0.28 mmol used)	vitrification time ± standard deviation/min	yield ± standard deviation (%)	T_g ± standard deviation/°C
DVB	50:50	135	none	57.0 ± 0.0	91.7 ± 1.2	89.9 ± 0.3
			$Zn(DEDC)_2$	40.3 ± 0.5	94.1 ± 0.7	94.4 ± 1.0
	70:30		none	33.0 ± 0.8	93.9 ± 0.2	46.2 ± 1.1
			$Zn(DEDC)_2$	21.7 ± 0.5	95.3 ± 0.1	34.8 ± 0.3
	30:70		none	109.0 ± 0.0	80.5 ± 0.3	83.3 ± 0.9
			$Zn(DEDC)_2$	98.0 ± 0.8	84.7 ± 0.5	82.4 ± 0.7
DIB	50:50	160	none	32 ± 0.0	92.1 ± 0.3	4.99 ± 0.63
			$Zn(DEDC)_2$	16 ± 0.0	92.5 ± 0.1	2.30 ± 1.17
		135	none	158	79.0	21.6
			$Zn(DMDC)_2$	70	85.1	26.6
			Na(DEDC)	126	77.9	14.9
			KEtX	129	75.4	18.6
			2-MBT	154	82.6	29.3
			dioctylamine	146	86.4	29.4
DCPD		135	none	220	60.0	45.2
			$Zn(DMDC)_2$	58	94.7	111.6
			Na(DEDC)	155	88.7	79.2
			KEtX	175	66.2	57.0
			2-MBT	194	68.9	68.3
			dioctylamine	164	76.3	77.4
EGDMA		160	none	134	82.8	unclear
			$Zn(DMDC)_2$	74	90.1	10.6
			Na(DEDC)	103	86.9	5.5
			KEtX	94	84.6	5.5
			2-MBT	135	82.3	7.6
			dioctylamine	121	81.7	6.9

[a]Where standard deviations are not provided, the reaction was not performed in triplicate.

moieties, hampering their nucleophilicity and any phase transfer agent behavior. Consistent with dodecanethiol, which was nonionic, both guanidine and thiourea, which are also nonionic, gave yields lower than that of uncatalyzed inverse vulcanization, suggesting that they too are promoting hydrogen sulfide formation. Because of this, the reaction using guanidine as a catalyst was repeated under gas capture conditions. Although the amount of hydrogen sulfide given off was found to be higher than that for the uncatalyzed inverse vulcanization of DVB, (1.51 vs 1.44 mmol of H_2S), the standard deviation in the result for the guanidine-catalyzed reaction is too large to say for certain that guanidine promotes the formation of hydrogen sulfide (Figure S12).

Moreover, a complement of amines were tested in this work to benchmark them against other catalysts, since Pyun et al. reported nucleophilic activation of inverse vulcanization by means of amines, and amines have been shown to cleave sulfur−sulfur bonds.[10,26,27] Dodecylamine, dioctylamine, and 1,4-diazabicyclo[2.2.2]octane (DABCO) were chosen as representative examples of primary, secondary, and tertiary amines, respectively. Conveniently, dodecylamine has an alkyl chain of length equivalent to that of dodecanethiol; thus, a comparison of the two is appropriate. Of the two, dodecylamine was the superior catalyst in terms of vitrification time, yield, and T_g, indicating that a sulfur atom is not necessary to provide nucleophilic activation. This is perhaps because as dodecylamine is a more powerful nucleophile than dodecanethiol it saw a greater rate enhancement. The greater reactivity of dodecylamine may have allowed the catalytic pathway to better compete with the pathway responsible for hydrogen sulfide formation, leading to the higher yield observed. It is, however, worth noting that dodecylamine gave a yield lower than that of uncatalyzed inverse vulcanization, so while it may be better at suppressing hydrogen sulfide formation in comparison dodecanethiol, it is still promoting hydrogen sulfide formation.

Of the amine catalysts/nucleophilic activators tested, dioctylamine was particularly effective in giving rapid reactions and maintained a yield comparable to that of uncatalyzed inverse vulcanization but fell short in providing high T_g values. Similarly, DABCO provided a good rate enhancement and a yield that was statistically insignificant from that of uncatalyzed inverse vulcanization, though the T_g value of the product polymer was more than 8 °C lower than that of an uncatalyzed polymer. These low T_g values are attributed to the relatively large molecular profile of the catalysts, particularly DABCO, which is rigid and bulky in all three dimensions and lacks the ability to unravel and extend its hydrocarbon units, unlike the other catalysts. This may disrupt the structure of the polymers and decrease the number of interchain interactions that would normally hold them together, leading to a lower T_g value. It should be noted that the use of amines as catalysts in inverse vulcanization is complicated by the fact that they have the potential to form thioamide groups.[44] It has been reported that primary amines can react directly with sulfur, to form thioamides, and that primary and secondary amines can react with sulfur and an alkyne to form thioamides, all of which can occur at temperatures lower than that of inverse vulcanization. Whether thioamides are forming here as a result of the

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presence of amines, and their effect upon the product polymers if they are forming, is unclear.

Versatility of Catalytic Inverse Vulcanization. To test the resilience of catalytic inverse vulcanization to variation under the reaction conditions, and its flexibility across different kinds of cross-linkers, a small selection of catalysts was assessed against reactions of several different organic comonomers. 1,3-Diisopropenylbenzene (DIB) was selected for its similarity to DVB. Dicyclopentadiene (DCPD) was selected because it is not aromatic and is structurally dissimilar to DVB. Ethylene glycol dimethacrylate (EGDMA) was selected because it is a representative example of a comonomer that contains heteroatoms which are in conjugation with the carbon−carbon double bond and because it has poor reactivity without a catalyst.[11] These experiments were performed to determine whether the conclusions of the catalytic trials upon the inverse vulcanization of DVB were applicable to other cross-linkers. Table 3 shows that in almost all cases the addition of a catalyst enhanced the vitrification time, yield, and T_g values and that the results mirrored those of the catalytic trials in terms of which catalysts were better and worse. The only exception to this was Na(DEDC), which was less effective than Zn(DMDC)$_2$ when it was used with the alternative cross-linkers, which is in agreement with the findings of Wu et al. in that Na(DEDC) was previously found to not be compatible with all organic comonomers.[11] Since in the work of Wu et al., reactions with EGDMA took long times to reach completion at 135 °C, the EGDMA reactions here were performed at 160 °C, to provide shorter vitrification times that were feasible to measure. At 160 °C the sulfur−EGDMA reaction mixture still vitrified without a catalyst, but the resultant polymer was unstable to depolymerization upon cooling. Only the inverse vulcanization of EGDMA with Zn(DMDC)$_2$ as a catalyst formed a stable polymer with a homogeneous structure. All of the EGDMA inverse vulcanized polymers, except that which was synthesized with the Zn(DMDC)$_2$ catalyst, showed numerous irregular features in their DSC thermograms (Figure S19), alluding to an inhomogeneous and poorly formed polymer structure, as well as characteristic peaks of elemental sulfur. The reaction using Zn(DMDC)$_2$ as a catalyst gave a DSC thermogram with only a T_g transition, indicating that it is the only completely successful catalyst for EGDMA.

The inverse vulcanization of DVB was performed at varied mass ratios of DVB to sulfur. In almost all cases, the addition of 0.28 mmol of Zn(DEDC)$_2$ to a 135 °C reaction gave the benefits of lower vitrification times, higher yields, and higher T_g values, as can be seen in Table 3. To further demonstrate the versatility of catalytic inverse vulcanization, the inverse vulcanization of DVB and sulfur at a 50:50 mass ratio was tested at 160 °C; however, this led to the Trommsdorff−Norrish effect. It was noted that, with a greater amount of DVB, the vitrification time was longer; therefore, the inverse vulcanization of DVB and sulfur in a 70:30 mass ratio was carried out. The reaction did not exhibit the Trommsdorff−Norrish effect; however, when the reaction was repeated with 0.28 mmol of Zn(DEDC)$_2$, the Trommsdorff−Norrish effect was observed. This indicates that introducing a catalyst into a reaction which is expected to be rapid (due to a highly reactive cross-linker and/or high temperature) is not beneficial, as it accelerates the reaction too much. To demonstrate that catalytic inverse vulcanization can be beneficial at higher temperatures when a less reactive cross-linker is used, the inverse vulcanization of DIB, which is less reactive than DVB, and sulfur at a 50:50 mass ratio was tested at 160 °C with and without 0.28 mmol of Zn(DEDC)$_2$. The results shown in Table 3 indicate that catalysis is indeed beneficial at higher temperatures with this cross-linker. This emphasizes the need for the thoughtful application of catalysis in inverse vulcanizations, as adding too much catalyst or adding a catalyst to an already rapid reaction has been demonstrated here to be detrimental. Note that, over the course of the overnight curing at 160 °C, the DIB polymers degraded from a solid to a liquid, indicating a drop in T_g. This degradation appears to have affected the catalyzed reaction more significantly, explaining its slightly lower T_g. The degradation could likely be avoided with optimization of the curing process.

CONCLUSIONS

In conclusion, it has been demonstrated here that catalytic inverse vulcanization is a versatile and beneficial technique in terms of producing higher quality inverse vulcanized polymers, in less time and in higher yield. Catalytic inverse vulcanization has been demonstrated with a variety of representative cross-linkers and catalysts. A wide range of metal diethyldithiocarbamates were shown to be reliable catalysts, as they provided increases in rate, yield, and glass transition temperature. Several other organic and organometallic species have also been shown to enhance the rate, yield, and glass transition temperature. More significantly, a library of catalysts for inverse vulcanization has been explored which allows easy comparison and selection of the catalysts, on the basis of several variables that were tested here. Copper(II) diethyldithiocarbamate gave the greatest performance of all of the tested catalysts, if equal weighting is given to the three factors of rate, yield, and T_g. If only the time required to reach vitrification is considered, then potassium isopropyl xanthogenate or potassium dodecanethiol, both in the presence of 18-crown-6 ether, gave the greatest enhancement. However, in commercial terms the relative cost of each catalyst will be a consideration, and excessively rapid rates may cause processing challenges, and so the choice of catalyst will be a compromise of several factors. Zinc(II) dimethyldithiocarbamate is as an ideal candidate for catalytic inverse vulcanization, on account of its better than average rate enhancement, yield, and glass transition temperature, while also being remarkably cost effective at the same time, and compatible to different comonomers; therefore it is recommended by the authors. In the compilation of this library of catalysts, several tentative conclusions about the mechanism of catalytic inverse vulcanization have been drawn. Sulfur monomer binding by the catalyst may be an important step in the reaction but is not inherently necessary to achieve a rate enhancement. Where sulfur monomer binding is present as a mechanistic step, it is plausible that the ion softness and LUMO energy may influence the behavior of catalysts with a metal cation. Conversely, it seems that coordination of the organic comonomers by their alkene π orbitals is not present as a mechanistic step, as no evidence could be found by NMR or computational studies. It was found that the catalysts may behave as nucleophiles, lowering the bond dissociation energy of the initial cleavage of S−S bonds in the reaction, and this action can be hampered if the reaction mixture is acidified. It was found that catalysts which may be prone to acting as bases could promote hydrogen sulfide formation, explaining the lower yields in these cases. Evidence has been found that the catalysts may act as phase transfer agents, as longer alkyl chains

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make them more soluble in the organic phase and enhance the rate of the reaction. This may better allow them to draw bound sulfur chains out of the molten sulfur phase and into the comonomer phase. Additionally, metal polysulfide complexes as catalytic intermediates have been further confirmed as a useful avenue of research in the mechanism of catalytic inverse vulcanization. To determine the exact mechanistic nature of catalytic inverse vulcanization is challenging, especially because of the insolubility of the products and difficulty in characterizing their exact structure. This is not unlike the similar challenges of determining the nature of the catalysis/acceleration of conventional vulcanization, a matter still under debate despite its long history and widespread industrial use. Rather, this work aimed to provide additional data and expand the previously small library of reported cases and to identify potential mechanistic steps for future study, while highlighting what factors affect catalyst efficiency.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c05010.

General considerations, experimental setup, solubility studies, method for inverse vulcanization, evaporation experiments, NMR kinetics study, evidence for the formation of potassium dodecanethiolate, synthetic procedure and analysis for $Mn(DEDC)_2$, synthetic procedure and analysis for $Zn(DODC)_2$, results of the gas capture reactions, representative analytical data for some inverse vulcanized polymers, results of the catalyst trials, PXRD of metal polysulfides, electrochemistry of the first-row transition-metal DEDCs, computational chemistry of the first-row transition-metal DEDCs, computational chemistry of the nucleophilicity of S_4^{2-}, and references (PDF)

Recording of a typical vitrification event (MP4)

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Notes

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